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A New Method for Provenance Determination of Metals by Analyzing Samples using Process of Electromigration

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A new method for Provenance determination of metals by analyzing samples using process of Electromigration.

Field of Application

This invention has direct application to Conflict Minerals programs and due diligence strategy to comply with Section 1502 of the Dodd Frank Wall Street Reform and Consumer Protection Act. It provides a novel method for establishing the provenance determination of certain metals and traceability of their mineral origins.

Background

This invention provides a technique for provenance determination of materials (e.g., minerals) and is useful for a variety of reasons. For example, materials from one location may be less valuable than those from another location or materials from one location may be more restrictive due to current laws of the land.

Laws restricting the sale of materials from certain areas may exist due to geopolitical concerns. Currently, distinguishing between particular conflict ore deposits (e.g., ores of Tin, Tantalum, Tungsten and Gold) requires a combination of mineralogical, geochemical and geochronological analyses, research and auditing, which can be both time consuming and human resource intensive.

Electromigration is the transport of material caused by the gradual movement of the ions in a conductor due to the momentum transfer between conducting electrons and diffusing metal atoms. Electromigration can take place in a metal sample by diffusion in the bulk, along metal surfaces or along grain boundaries. The bulk diffusion dominated electromigration is purely dependent on the type of material and not suitable for mineral provenance. Surface diffusion dominated electromigration depends on the sample preparation and encapsulation conditions and also not suitable for mineral provenance. Electromigration dominated by grain boundary diffusion is suitable for mineral provenance. The grain boundaries are where grains meet in a solid. Grain boundaries are transition regions between the neighboring crystals where there is a disturbance in the atomic packing. Grain boundaries can act as sources and sinks for vacancies at high temperatures, leading to diffusion currents that cause can cause electromigration. In polycrystalline materials, the individual grains usually have a random orientation with respect to one another. Research has shown that the activation energy for grain boundary dominated electromigration is unique to the origin of the metal. It has also been shown that melting and smelting of metals can change the grain boundary size and orientations but they do not change the electromigration activation energy that is dominated by grain boundary diffusion. This property is used in this invention for mineral provenance determination.

Prior Work:

Generally, provenance methods can be sorted into two categories, which are petrological methods and geochemical methods. Examples of petrological methods include QFL ternary diagram, reworked fossils and stock magnetic properties. Examples of geochemical methods include zircon U-Pb dating, zircon fission track, apatite fission track, bulk sediment Nd and Sr isotopes, etc. These solutions are not suitable for

provenance determination of metals and their mineral origins. They are more suitable for determination of Thermochronological age of the samples.

Method:

A method for analyzing a sample by passing a very high current density into a sample, introducing the process of electromigration in the sample, recording electromigration parameters, determining the electromigration activation energy from the parameters and comparing the measured activation energy of the sample to a reference library wherein each reference sample activation energy and its corresponding provenance information is used for provenance determination of the analyzed sample.

For consistency and for accurate comparison of measured activation energies with the activation energies of known reference samples, the sample preparation of the analyzing sample must be identical to the reference sample.

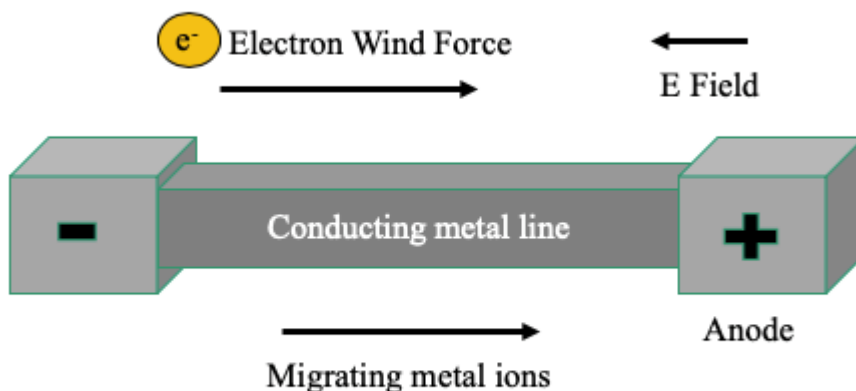
The activation energy depends strongly on the diffusion mechanism. Diffusion can proceed through the lattice, or grain boundaries, and along interfaces or the surface. The lattice is the most difficult path with the highest activation energy followed by the grain boundary and then the surface. In some metals, the surface is generally not available due to the presence of a coherent oxide film. Interfacial diffusion activation energies differ for every interface and can be either greater or less than that for grain boundary diffusion. Adding alloying elements generally has the paradoxical effect of decreasing the lattice and increasing the grain boundary activation energies.

Method for analyzing a sample

The method of preparing and analyzing a metal sample for provenance determination using process of Electromigration is described. The focus of this method is for the current conflict mineral metals of Sn (Tin), Ti (Titanium), Ta (Tantalum) and Au (Gold), however this method can be extended to other metals of relevance. These 4 metals are abbreviated as 3TG.

Experimental Test Structure:

Dog bone shaped metal lines are designed on a PCB as follows:



Dog bone shaped lines on the PCB are conducting metal lines.

The length, width and thickness of the metal line can vary. A typical length can be a few millimeters.

Lines too small in length can result in Bleach effect (I. Blech: *Electromigration in Thin Aluminum Films on Titanium Nitride*. Journal of Applied Physics, Vol 47, pp. 1203-1208, April 1976.) and should therefore be avoided.

The cross-sectional area of the metal line will determine the absolute amount of current needed to stress the metal line. The recommended current density is 10^6 Amperes / Square centimeters.

Line Width (cm)	Cross-sectional area (square cm)	Current* in Amperes
0.1	0.01	10000
0.01	0.0001	100
0.001	0.000001	1

*Current needed for current density of 10^6 Amperes / Square centimeters.

The activation energies for electromigration for each metal sample from a known smelter must be individually determined. Such activation energies will be used as reference measurements for comparison with metal samples of unknown origin for provenance determination. For each metal the activation energy for electromigration will be unique to its origin because the metal and the intrinsic impurities are specific to the origin of the metal (its provenance).

Activation Energy:

Electromigration is the phenomenon of migrating metal ions under very high current densities. It leads to void formation in the conducting metal lines that result in open circuits (failure of a line). A failure can be defined as an increase in line resistance by 25%. It has been shown empirically by J.R. Black (Black, J.R., Proc. 6th Ann. Intl. Reliab. Phys. Symp., 148, 1967. ([Google Scholar](#)), that the Median time for failure of a conducting metal line under high current densities follows an Arrhenius relationship:

$$MTTF = \frac{A}{J^2} \exp\left(\frac{E_a}{kT}\right)$$

J = Electrical Current density

T = Metal Temperature (degrees Kelvin)

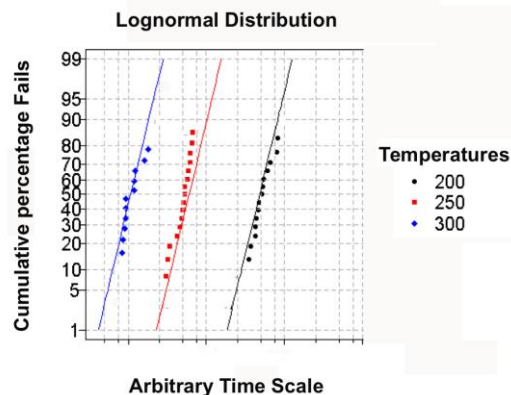
A = Cross-sectional area of the metal line

E_a = Activation in electron volts

K = Boltzmann's constant

Determination of Activation Energy:

The Activation energy can be determined empirically by stressing a metal line at multiple temperatures but using the same current density. The recommended temperatures are 200, 250 or 300 degrees Celsius but will vary depending on the metal type. The recommended sample size for each temperature is 20 samples. The recommended current density is 10⁶ Amperes / Square centimeters.



The Median Time to Fail (MTTF) is the failure time for 50% of the sample population in the distribution.

$$\frac{MTTF_{200}}{MTTF_{300}} = \exp\left(\frac{E_a}{K} \left(\frac{1}{(200+273)} - \frac{1}{(300+273)} \right)\right)$$

Activation Energy for each metal, E_a, can therefore be determined by solving for E_a (the only unknown) .

Database of Activation Energies:

With known source of each metal (each 3TG metal) a reference database of activation energies can be experimentally determined as tabulated below:

Metal	Source Location	Activation Energy (ev)
Tin	Loc Sn-1	Ea-Sn-1
Tin	Loc Sn-2	Ea-Sn-2
Tin	Loc Sn-3	Ea-Sn-3
Tin	Loc Sn-4	Ea-Sn-4
Tin	Loc Sn-5	Ea-Sn-5
Titanium	Loc Ti-1	Ea-Ti-1
Titanium	Loc Ti-2	Ea-Ti-2
Titanium	Loc Ti-3	Ea-Ti-3
Titanium	Loc Ti-4	Ea-Ti-4
Titanium	Loc Ti-5	Ea-Ti-5
Tantalum	Loc Ta-1	Ea-Ta-1
Tantalum	Loc Ta-2	Ea-Ta-2
Tantalum	Loc Ta-3	Ea-Ta-3
Tantalum	Loc Ta-4	Ea-Ta-4
Tantalum	Loc Ta-5	Ea-Ta-5
Gold	Loc Au-1	Ea-Au-1
Gold	Loc Au-2	Ea-Au-2
Gold	Loc Au-3	Ea-Au-3
Gold	Loc Au-4	Ea-Au-4
Gold	Loc Au-5	Ea-Au-5

Each 3TG metal is obtained from its specific mining/smelter location and by nature its impurity concentration will be uniquely determined by its mining location and/or smelter. The activation energy will be unique to each metal and its source location because it is a strong function of the metal and the impurities in the metal. In this invention, the exact composition of the impurities is not necessary to be determined because it correlates directly to the activation energy for electromigration. There are hundreds of mines and smelters in the world for each 3TG metal and the proposed method establishes an efficient way to store the measured electromigration activation energies for reference.

Provenance determination of sample metal of unknown source /origin:

The above steps can be applied on a sample metal of unknown origin. Sufficient homogenous content of the metal of unknown provenance must be collected and used for creating a test structure as described. The activation energy determined experimentally can be compared to the known source metal activation energies database in order to establish a match to a known location and therefore its provenance.

The use of metal electromigration activation energies to establish provenance determination of the metal has never been reported and as such this is a new and unique method to establish the unknown provenance of metals.

Conclusion:

The invention is a novel way of determination of provenance of metal by mapping measured material properties (Activation energy for Electromigration) to known samples from known geographical location of origin.

Its practical use is proposed to be a tool to establish legitimacy of origin and sourcing of metals.

This will have direct application in due-diligence enforcement for Conflict Minerals tracing and tracking to their mines of origin.

A NEW METHOD FOR PROVENANCE
DETERMINATION OF METALS BY
ANALYZING SAMPLES USING PROCESS
OF ELECTROMIGRATION

ACRONYMS / SYMBOLS

- **PD** – Provenance Determination
- **3TG** - Sn (Tin), Ti (Titanium), Ta (Tantalum) and Au (Gold) - These 4 metals are abbreviated as 3TG
- **CM** – Conflict Minerals
- **EM** – Electromigration
- **E_a** – Activation Energy
- **J** – Current Density
- **FA / FI** – Failure Analysis / Failure Identification
- **(M)TTF** – (Median) Time to Fail
- **BKM** – Best Known Methodology
- **GB** – Grain Boundary

SUMMARY

- Background:
- What is Provenance Determination (PD) ?
- Invention Relevance to Industry
- What is Electromigration ?
- Description of Invention
- Conclusion

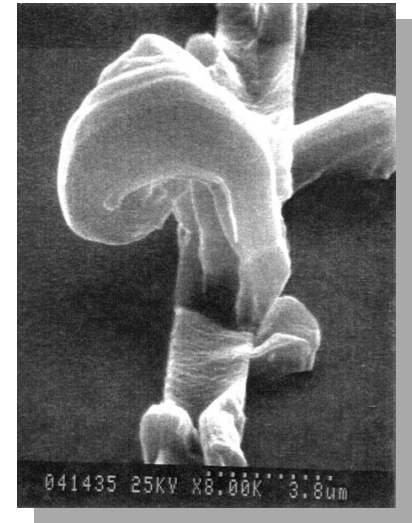
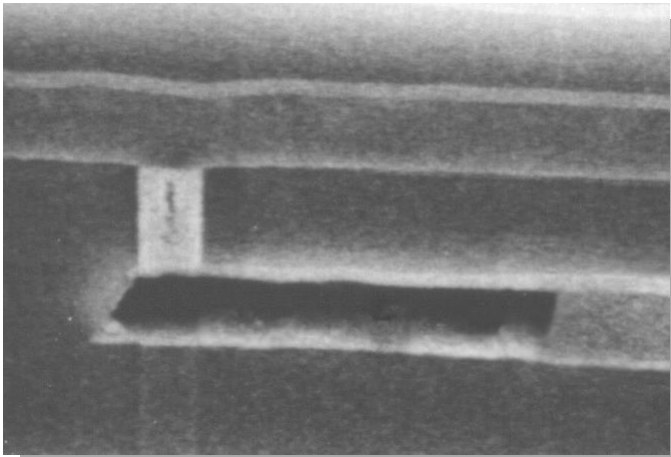
WHAT IS PROVENANCE DETERMINATION (PD)?

- “Provenance” deals with the question of where a material originates from
- Historically for Rocks and Sediments but broadly for naturally occurring materials including metals
- Goal of PD is to determine source of material by analyzing microstructure or material properties
- Not for establishing age of materials (not C dating)
- **Focus of this Invention to use one such property of metals (EM Activation energy) for a novel methodology for PD**

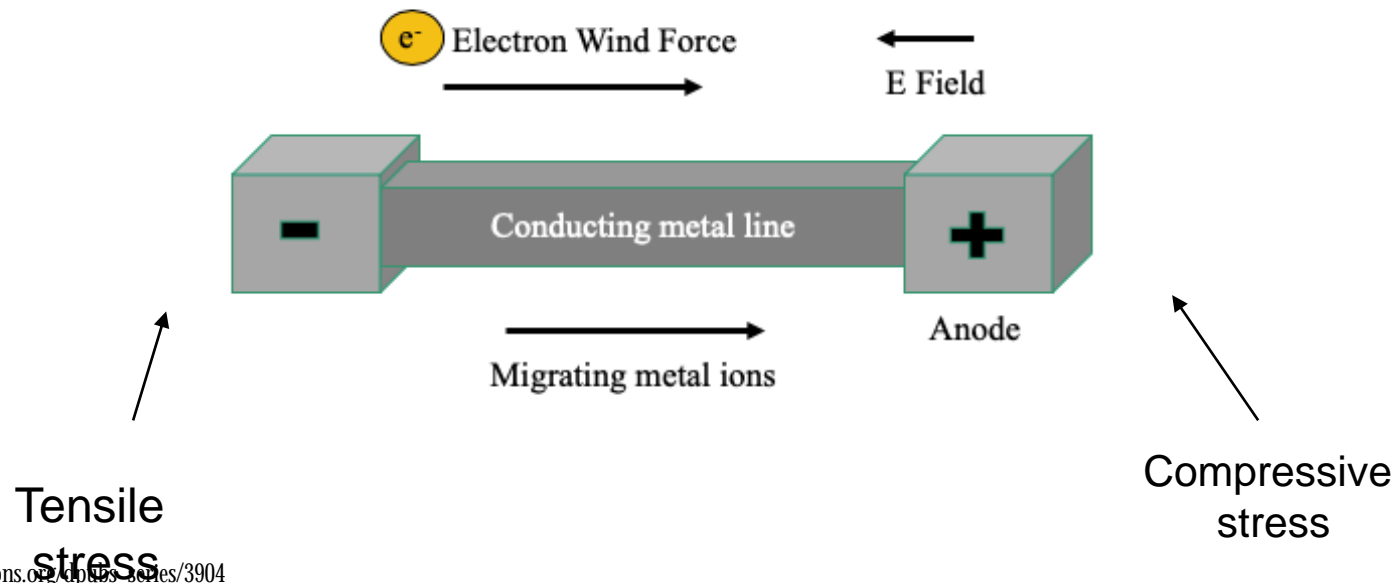
INVENTION RELEVANCE

- Direct application to current Industry Conflict Minerals (CM) program (Section 1502 of the Dodd Frank Act)
- Metals in focus for CM: Sn (Tin), Ti (Titanium), Ta (Tantalum) and Au (Gold) -3TG
- Laws restricting the sale of materials from certain areas exist due to geopolitical concerns.
- Currently Industry BKM requires a combination of mineralogical, geochemical and geochronological methods*
(<https://doi.org/10.1306/D42677FD-2B26-11D7-8648000102C1865D>)
- Analyses, research and auditing – time consuming
- **The use of metal electromigration activation energies to establish provenance determination of the metal has never been reported**
- Proposing a Novel method for establishing the provenance determination of certain metals using experimental electromigration activation energy determination.

WHAT IS ELECTROMIGRATION ?



(Cho 1990)



WHAT IS ELECTROMIGRATION ?

- **Basics: Metal lattice ion migration under High current densities**
- Migration is net transport of metal ions in a conductor
- The space an ion leaves behind is a vacancy
- Diffusion is migration
- The easiest way for an ion to move is to change places with a vacancy in the metal lattice
- Analogy: Think Hurricane Katrina – Just wind blowing, but...can do major damage over time
- **Huge flux of electrons in a metal causes ions to move in a preferential direction**
- Typically happens in Integrated circuits and PCBs

ELECTROMIGRATION FAILURE MODEL

- **Black's law:** $MTTF = \frac{A}{J^n} \exp\left(\frac{E_a}{kT}\right)$
- An Empirical Model – known for last 60 years
- TTF = time to failure (Median TTF, statistically speaking)
- A is a constant that is dependent on structure
- J is current density in the conducting metal line
- n varies between 1 and 2 (exponent for J)
- E_a is activation energy for electromigration (ev)
- k is Boltzmann's constant
- T is temperature in degrees K

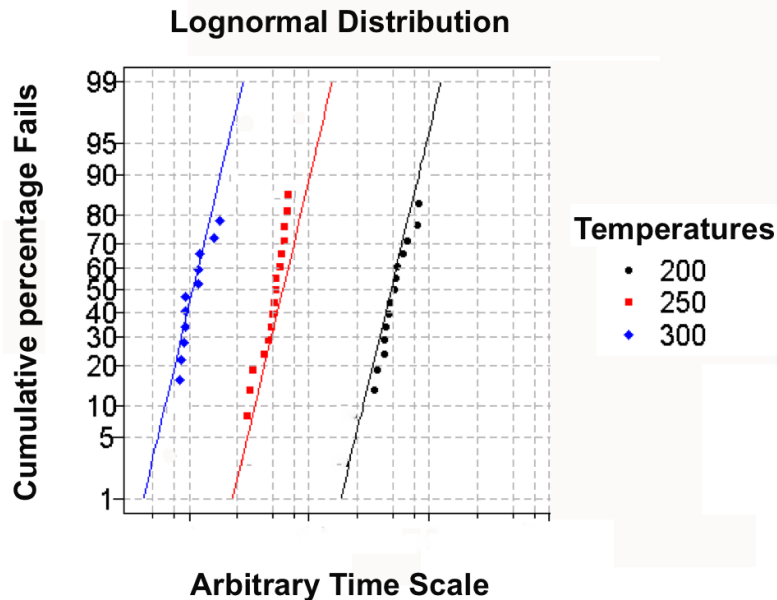
WHY EM ACTIVATION ENERGY FOR PD ?

- An Intrinsic property of a pure Metal
- Very sensitive to level of impurities
- Sensitive to modes of diffusion (eg Bulk vs GB vs Int)
- Can easily correlate/determine EM mode using FA
- Every metal from a unique smelter is unique in its impurities and EM activation energy
- A de-facto metal provenance by EM - E_a fingerprinting

DETAILS

- Electromigration Activation Energy*
- Determined empirically* by stressing a metal line at multiple temperatures and high J
- $J \sim 10^6$ A/square cms

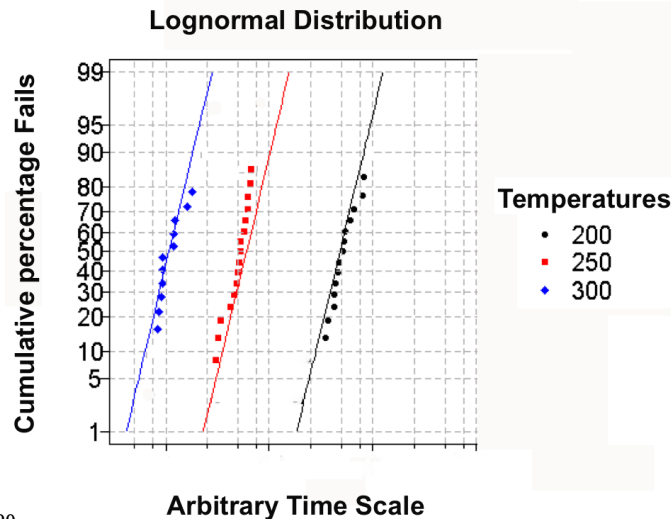
*For dominant mode of diffusion



DETAILS- CONTD...

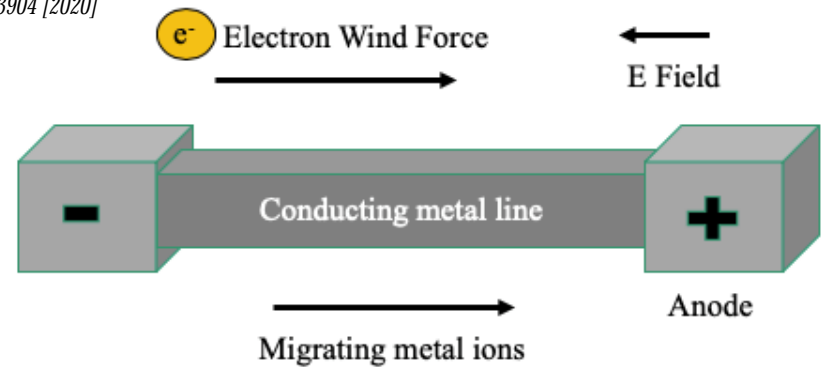
- The Median Time to Fail (MTTF) is the failure time for 50% of the sample population in the distribution.
- Activation Energy for each metal, E_a , can therefore be determined by solving for E_a (the only unknown) .

$$\frac{MTTF_{200}}{MTTF_{300}} = \exp \frac{E_a}{K} \left(\frac{1}{(200+273)} - \frac{1}{(300+273)} \right) |$$



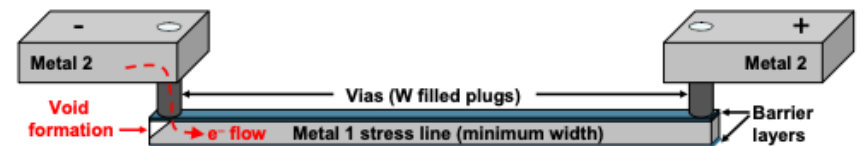
DETAILS- CONTD...

- Experimental Test Structure:
- Dog bone shaped metal lines can be designed on PCB or NIST* recommended test micro-structures fab-ed on Si
- The length, width and thickness of the metal line can vary. A typical length can be a few millimeters.
- Lines too small in length can result in Blech effect*
- The cross-sectional area of the metal line will determine the absolute amount of current needed



Line Width (cm)	Cross-sectional area (square cm)	Current* in Amperes
0.1	0.01	10000
0.01	0.0001	100
0.001	0.000001	1

*Current needed for current density of 10^6 Amperes / Square centimeters.



A two-level metal via electromigration test structure illustration.

J typical for NIST structures in mA / square microns *NIST.gov

* I. Blech: *Electromigration in Thin Aluminum Films on Titanium Nitride*. Journal of Applied Physics, Vol 47, pp. 1203-1208, April 1976.
https://www.tdcommons.org/dpubs_series/3904

DETAILS– CONTD...

- With known source of each metal a reference database of activation energies can be experimentally determined as tabulated:

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Tin	Loc Sn-5	Ea-Sn-5
Titanium	Loc Ti-1	Ea-Ti-1
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Tantalum	Loc Ta-2	Ea-Ta-2
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Gold	Loc Au-2	Ea-Au-2
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Gold	Loc Au-4	Ea-Au-4
Gold	Loc Au-5	Ea-Au-5

DETAILS – CONTD...

- Each 3TG metal sample is obtained from its specific mining/smelter location
- Metal's impurity concentration uniquely determined by its mining location and/or smelter.
- The activation energy will be unique to each metal and its source location because it is a strong function of the metal and the impurities in the metal (intrinsic and extrinsic)
- Exact composition of the impurities is not necessary to be determined
- Correlates directly to the activation energy for electromigration.
- The proposed method establishes an efficient way to store the measured electromigration activation energies for reference.

INVENTION SUMMARY

- Phenomenon of Electromigration, Black's Law model and activation energies are well established from 1960's
- US and EU regulation for 3TG metal sourcing puts extra burden for NGO and Government enforcement
- Provenance determination of metal origin (mine / smelter) is currently complicated and time consuming
- Metal microstructure and EM properties correlate to their provenance
- **Use of EM Activation energy to establish Metal Provenance is Novel**
- A new and unique method to establish the unknown provenance of metals